Nonlinearities in composition dependence of structure parameters and magnetic properties of nanocrystalline fcc/bcc-mixed Co-Ni-Fe thin films

Chechenin, N. G.; Khomenko, E. V.; Vainchtein, D. I.; de Hosson, J. Th. M.

Published in:
Journal of Applied Physics

DOI:
10.1063/1.2884120

Nonlinearities in composition dependence of structure parameters and magnetic properties of nanocrystalline fcc/bcc-mixed Co–Ni–Fe thin films

N. G. Chechenin,[1,a)] E. V. Khomenko,[1] D. I. Vainchtein,[2] and J. Th. M. De Hosson[2]
[1]*Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University, 119991 Moscow, Russia*
[2]*Department of Applied Physics, University of Groningen, Nijenborgh 4, NL 9747 AG Groningen, The Netherlands*

(Presented on 9 November 2007; received 12 September 2007; accepted 31 January 2008; published online 24 March 2008)

In this report, the nonlinearities are analyzed in fcc-to-bcc (fcc/bcc) population ratio, lattice parameters ($a_{\mathrm{exp}}^{\mathrm{fcc}}/a_{\mathrm{ideal}}^{\mathrm{fcc}}$ and $a_{\mathrm{exp}}^{\mathrm{bcc}}/a_{\mathrm{ideal}}^{\mathrm{bcc}}$) and saturation magnetization (I_S^{obs}/I_S^a) of the electrodeposited thin Co–Fe–Ni films as a function of average number of electrons in the alloy (n_e), which proved to be a convenient way to follow the variation of chemical composition. The enhancement of the saturation magnetization correlated with the nonlinear deformation and connected with a complicated rearrangement of the outer shell electron configurations due to change in composition in a disordered alloy. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2884120]

I. INTRODUCTION

In various applications, such as magnetic recording systems, high frequency planar inductors, and modern nonvolatile magnetic memory, soft magnetic thin films with a high magnetic moment are required. Most often, the Permalloy is used for this purpose, which has a very low coercivity, however, a modest magnetization in saturation. It is proved that Co–Ni–Fe ternary alloy can possess a much higher saturation magnetization.[1] It is also known that at a certain deposition condition Co–Ni–Fe film can contain two structural phases, fcc and bcc, which competition decreases the coercive force and magnetostriction.[2] At the same time, a complicated correlation between deposition condition, microstructure, and magnetic properties is the basic constraint of the industrial application of this material. In this paper, we analyze the structure, lattice parameters, and saturation magnetization of the electrodeposited thin Co–Fe–Ni films as a function of chemical composition. We discovered clear correlations between nonlinearities in the structure and saturation magnetization and discuss the origin of these correlations.

II. EXPERIMENT

Nanocrystalline Co–Ni–Fe films were prepared by the electrochemical method on Cu(250 nm)/Cr(25 nm)/SiO_2(300 nm)/Si substrate.[2] The recipe of the electrochemical bath was essentially the same as in Ref. 3. Uniaxial magnetic anisotropy was obtained applying a permanent magnetic field around of 800 Oe during the film deposition. The deposited film thickness was in the range of 50–220 nm as measured by the Rutherford backscattering technique. The chemical composition of the films was determined from the energy dispersive analysis of x-rays [scanning electron microscopy-energy dispersive spectroscopy (EDS) and transmission electron microscopy-EDS]. The concentrations of Co, Fe, and Ni varied between 0.30 and 0.54, 0.12 and 0.31, and 0.15 and 0.58, respectively. From x-ray diffraction (XRD) study, we have learned that the Co–Ni–Fe films are normally composed of fcc and bcc competing structural phases.[4] The fcc fraction and bcc fraction present in the alloy were obtained from the areas under the $(111)_{\mathrm{fcc}}$, A_{fcc} and $(200)_{\mathrm{bcc}}$, A_{bcc}, XRD lines, respectively. From the XRD linewidths, we estimated for the fcc phase that the grain size was about 30 nm for most of the samples, while it was about 10–20 nm for bcc grains.

The saturation magnetization I_S as well as the anisotropy field H_K were obtained from ferromagnetic resonance (FMR) measurements at the frequency $f=9.40$ GHz in an external magnetic field range of up to 5 kOe, comparing the resonance fields along easy (EA) and hard (HA) axes, and applying the Kittel relationships

$$\omega^2 = \gamma^2(H_R^{\mathrm{EA}} + H_k)(H_R^{\mathrm{EA}} + H_k + 4\pi I_s), \tag{1a}$$

$$\omega^2 = \gamma^2(H_R^{\mathrm{HA}} - H_k)(H_R^{\mathrm{HA}} - H_k + 4\pi I_s), \tag{1b}$$

where $\omega=2\pi f$ is the frequency of the applied rf field, $\gamma = ge/(2mc) \approx g \times 8.79 \times 10^6 (\mathrm{G\ s})^{-1}$ is the gyromagnetic ratio, and H_R^{EA} and H_R^{HA} are the resonance values of the dc field applied in the EA and HA directions, respectively. From FMR measurements, we obtained that the agreement between the tabulated and measured saturation magnetization for pure Co, Ni, and Fe films, grown in the same conditions and with similar thicknesses as for Co–Ni–Fe films, could be reached, assuming the g factors to be about 2.0 for these pure films. This value corresponds to the static $g=2$ for electrons with frozen orbital moments for monoatomic films and leave no reason to assume a larger g factor value for our Co–Ni–Fe films. With $g=2$ value, the saturation magnetization, depending on the composition, varied between $4\pi I_s = 16.7$ and 21 kG, which is a high value, compared to that of Permalloy. It has been shown that the saturation magnetization is quite

a)Author to whom correspondence should be addressed. chechenin@sinp.msu.ru. Tel: +7 495 939 2348. FAX: +7 495 939 0896.

sensitive to the chemical composition in Co–Ni–Fe.[1,5]

III. RESULTS

Normally, a ternary alloy composition dependence of alloy parameters is illustrated by triple diagrams. Here, to study the composition effects in a generalized way, we combine the two independent parameters of the composition of the ternary alloy into a single number of electrons per atom,

$$n_e = 27x + 28y + 26z,$$

where x, y, and z are the concentrations of Co, Ni, and Fe in the alloy, respectively, with $x+y+z=1$.

Figure 1(a) shows the natural logarithm of $A_{\mathrm{fcc}}/A_{\mathrm{bcc}}$ ratio as a function of the number of electrons per atom n_e of Co–Ni–Fe alloy. The dashed line is the line of the equal population of the fcc and bcc phases. A quite pronounced peak of $\ln(A_{\mathrm{fcc}}/A_{\mathrm{bcc}})$ is seen at around $n_e=27.0$, evidencing the dominance of the fcc phase. Increase of n_e above this value, i.e., decrease of Fe content, leads a surprising decrease of the fcc fraction and, further on, to a parity of the two phases. A reduction of n_e below 27.0, i.e., an increase of Fe content, leads to a single bcc phase which is the natural structure for α-Fe.

From the positions of the $(111)_{\mathrm{fcc}}$ and $(200)_{\mathrm{bcc}}$ lines, the lattice parameters $a_{\mathrm{exp}}^{\mathrm{fcc}}$ and $a_{\mathrm{exp}}^{\mathrm{bcc}}$ were obtained from the XRD data which varied also with the composition. In a simplest ideal solid solution case, the lattice parameter of a random binary alloy can follow the linear Vegard law,[6] if the pure components have the same type of the lattice. For ternary alloy with different structures of pure components (pure Co and Ni crystals have fcc while pure Fe preferably has the bcc structure), the experimental lattice parameter can be compared with a concentration weighted combination, based on atomic volumes per atom, as suggested by Zen.[7] Assuming that in both fcc and bcc phases, the volume per atom is the same and taking into account that there are two atoms in the bcc and four atoms in the fcc lattices, we write for ideal lattice parameters,

$$a_{\mathrm{ideal}}^{\mathrm{fcc}} = a_{\mathrm{Co}}^{\mathrm{fcc}}x + a_{\mathrm{Ni}}^{\mathrm{fcc}}y + \sqrt[3]{2}a_{\mathrm{Fe}}^{\mathrm{bcc}}z, \tag{2a}$$

$$a_{\mathrm{ideal}}^{\mathrm{bcc}} = \frac{1}{\sqrt[3]{2}}(a_{\mathrm{Co}}^{\mathrm{fcc}}x + a_{\mathrm{Ni}}^{\mathrm{fcc}}y) + a_{\mathrm{Fe}}^{\mathrm{bcc}}z. \tag{2b}$$

The ratios $a_{\mathrm{exp}}^{\mathrm{fcc}}/a_{\mathrm{ideal}}^{\mathrm{fcc}}$ and $a_{\mathrm{exp}}^{\mathrm{bcc}}/a_{\mathrm{ideal}}^{\mathrm{bcc}}$ of the experimental lattice parameters to the ideal anticipated ones as a function of composition in terms of number of electron per atom n_e are plotted in Figs. 1(b) and 1(c), respectively. The lattice parameters of fcc-Co, fcc-Ni, and bcc-Fe are equal to 3.544, 3.515, and 2.867 Å, respectively. The volume required per one atom in Fe is by about 5.9% larger than that per Co and by about 8.5% larger than that per Ni atoms. Therefore, the largest change of the $a_{\mathrm{ideal}}^{\mathrm{fcc}}$ alloy lattice parameter occurs when the concentration of Fe varies. Largest values of $a_{\mathrm{ideal}}^{\mathrm{fcc}}$ and $a_{\mathrm{ideal}}^{\mathrm{bcc}}$ are equal to 3.61 and 2.867 Å, respectively, corresponding to the dominance of Fe in the alloys.

The deviation of the ratios from the unity can be interpreted as a nonlinear deformation of the crystal lattice cells. When Fe concentration decreases, i.e., n_e increases, both, the bcc $a_{\mathrm{exp}}^{\mathrm{bcc}}$ and the fcc $a_{\mathrm{exp}}^{\mathrm{fcc}}$ lattice parameters decrease slower than those predicted by Eqs. (2a) and (2b), giving the effect

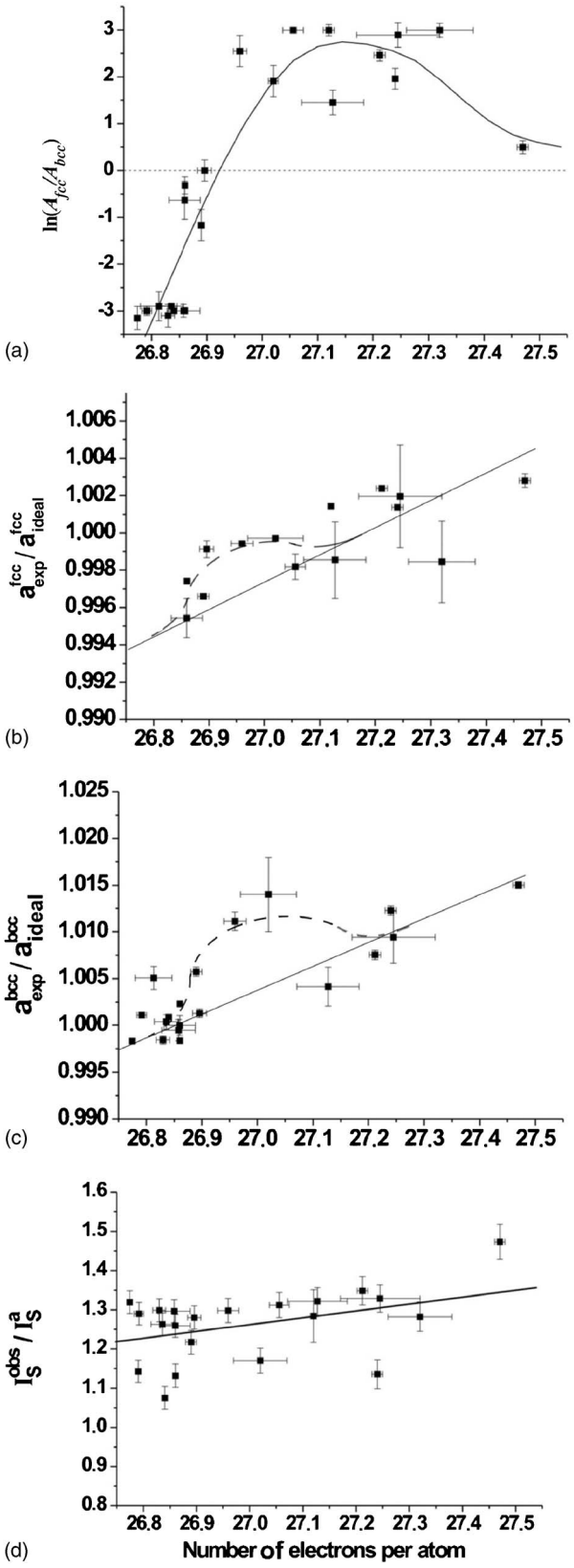

FIG. 1. Nonlinear variation of fcc/bcc ratio (a), lattice parameters of fcc (b), bcc (c) competing phases, and saturation magnetization (d) of Co–Ni–Fe nanocrystalline films as a function of composition expressed in terms of the average number of electrons per atom. Solid lines in (b)–(d) are fits to the data.

of an increase of the ratios $a_{\text{exp}}^{\text{bcc}}/a_{\text{ideal}}^{\text{bcc}}$ and $a_{\text{exp}}^{\text{fcc}}/a_{\text{ideal}}^{\text{fcc}}$ [Figs. 1(b) and 1(c)]. One can also note that pronounced bumps in the ratios $a_{\text{exp}}^{\text{bcc}}/a_{\text{ideal}}^{\text{bcc}}$ and $a_{\text{exp}}^{\text{fcc}}/a_{\text{ideal}}^{\text{fcc}}$ are around $n_e=27.0$, i.e., in the region of the peak in $\ln(A_{\text{fcc}}/A_{\text{bcc}})$ [Fig. 1(a)]. This latter effect of the second order nonlinearity in the lattice deformation could be qualitatively interpreted as a consequence of a kind of frustration in the transitional region between the bcc and the fcc phases, producing even more extent bonding in nanocrystals.

Similar to the ideal lattice parameters, one can compose an ideal anticipated saturation magnetization I_S^a of Co–Ni–Fe alloy as a linear combination of the partial magnetizations

$$I_S^a = I_S^{\text{Co}}x + I_S^{\text{Ni}}y + I_S^{\text{Fe}}z, \tag{3}$$

where the partial magnetic moments I_S^X of pure fcc-Co, fcc-Ni, and bcc-Fe are 1400, 480, and 1700 G, respectively. With such a representation, we can expect a variation of $4\pi I_S^a$ in the range of 11–17 kG for the variation of the composition in the investigated films. The observed $4\pi I_S^{\text{obs}}$ values diverge systematically from the anticipated values. One can see from Fig. 1(d) that the ratio I_S^{obs}/I_S^a is higher than the unity in all the composition range investigated, showing a tendency to increase with the increase at high n_e values. The data support the effect of enhancement of the observed saturation magnetization compared with the ideal anticipated values, especially for lower iron concentration or higher number of electrons per atom reported previously.[5]

IV. DISCUSSION AND CONCLUSIONS

A deviation from the Vegard law or from the Zen law for binary system is a common observation and there is no reason why these deviations could diminish in a ternary alloy. Evidently, this kind of nonlinear deformation is connected with a rearrangement of the outer shell electron configurations in a disordered alloy with the change in composition. For the case of competing nanocrystalline structural phases, there is an additional effect related to softening of the bcc bonds with the decrease of Fe content and increase of n_e in the alloy in the transition around $n_e=27$. The fcc grains start to nucleate in this region and with fcc bonds softer (and more extent) than for those anticipated from linear Zen's law [Eq. (2a)]. Since the competing bcc and fcc phases have spacing mismatch, there will be an interfacial effect, which could also cause nonlinear and an additional reconfiguration of the outer shell electrons. However, comparing the data, we can conclude that the internal (change in composition) and external (interface effect) induced electron reconfigurations have a different influence on magnetic properties of the alloy. While systematic nonlinearity, i.e., a general trend to increase of $a_{\text{exp}}^{\text{bcc}}/a_{\text{ideal}}^{\text{bcc}}$ and $a_{\text{exp}}^{\text{fcc}}/a_{\text{ideal}}^{\text{fcc}}$ with increase of n_e, correlates with the tendency to increase of I_S^{obs}/I_S^a, there is no a clear evidence of a strong effect of interface effect on I_S^{obs}/I_S^a,

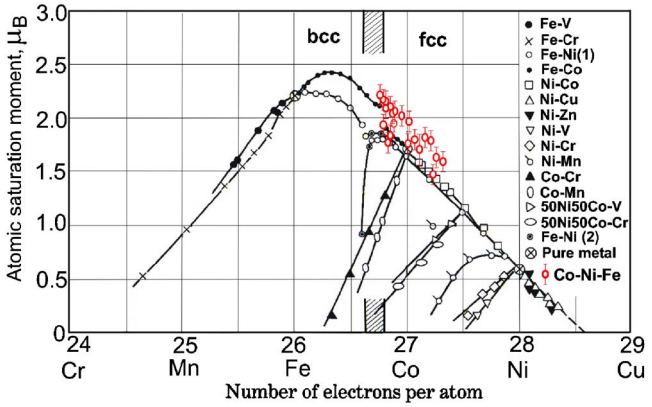

FIG. 2. (Color online) Slater–Pauling plot (Ref. 8) with our data for Co–Ni–Fe alloy shown as circles with error bars.

which definitely presents in the lattice parameter behavior. Moreover, from comparison of Figs. 1(a) and 1(d), we can conclude that the enhancement of saturation magnetization is more evident when the parity of the competing phases stabilizes.

The effect of enhancement of saturation magnetization is further illustrated in Fig. 2 in a comparison with previous data depicted in the Slater–Pauling plot.[8] In the Slater–Pauling plot, the effect of transitional element composition can be presented as a linear decrease of the magnetic moment from the value of $1.73\mu_B$ for Co to $0.61\mu_B$ for Ni. However, in the fcc-bcc phase transitional region, there is a large divergence of the experimental data from the linear decrease, both for previous and for our data. The enhancement of magnetic moment over the Slater–Pauling curve, in our case, we ascribe to the effect of rearrangement of the outer shell electron configurations in a disordered nanocrystalline alloy with the change in composition in the presence of competing fcc and bcc phases.

ACKNOWLEDGMENTS

This work is partially supported by the Grant Nos. GK-02.513.11.3285 and GK-02.513.11.317 of Russian Federal Agency on Science and Innovations.

[1]T. Osaka, M. Takai, K. Hayashi, K. Ohashi, M. Saito, and K. Yamada, Nature (London) **392**, 796 (1998).
[2]E. H. du Marchie van Voorthysen, F. T. Broek, N. G. Chechenin, and D. O. Boerma, J. Magn. Magn. Mater. **266**, 251 (2003).
[3]X. Liu, G. Zangari, and L. Shen, J. Appl. Phys. **87**, 5410 (2000).
[4]N. G. Chechenin, E. V. Khomenko, and J. Th. M. de Hosson, JETP Lett. **85**, 212 (2007).
[5]E. V. Khomenko, E. E. Shalyguina, and N. G. Chechenin, J. Magn. Magn. Mater. **316**, 451 (2007).
[6]L. Vegard, Z. Phys. **5**, 17 (1921).
[7]E. Zen, Am. Mineral. **41**, 523 (1956).
[8]S. Chikazumi, *Physics of Ferromagnetism* (Oxford University Press, Oxford, 1997).